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[54] Title of Invention: a Ziegler-type catalyst and its
preparation technique, which is applicable in the gas-phase
method ethylene polymerization process

[57] Abstract

This invention relates to a Ziegler-type catalyst and its
preparation techniques, which are applicable in gas-phase
method ethylene polymerization processes. The catalyst has
such characteristics as high activation, strong copolymerization
properties, and wide distribution of the product's molecular
weight. It may be used in ethylene gas-phase homo-
polymerization. It may be also used with α -alkene
copolymerization to produce low-pressure high-density
polymerizing ethylene or low-and-medium density
polymerizing ethylene.

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Claims

1. A Ziegler-type catalyst applicable in the gas-phase method ethylene polymerization process includes the following processes: impregnate the difficult-to-melt inorganic oxide support, the surface of which contains alkyl, into an inorganic chromium compound water solution, after being dried, roasted, and reduced, to produce the catalyst. The feature of the process is to adopt the organic aluminum compound as the reducer.
2. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said reducer is the organic aluminum compound with the following formula:



Whereas, R or R' is the alkyl of 1 ~ 20 carbon atoms. These two may be the same or different; x or y is the integral number ranging from 1 to 3. These two may be same or different.

3. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said organic aluminum reducer is the organic aluminum compound such as AlR_3 and ROIR'_2 .
4. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said organic aluminum reducer may also be the partial water solution of the alkyl aluminum compound such as MAO, EAO, BAO, i-BAO, and EBAO.
5. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said inorganic oxide support are SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and TiO_2 .
6. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that, among the said inorganic oxide support, the oxidized silica support is better.
7. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said inorganic chromium compounds include chromium oxide, inorganic salt, acetate, oxalate, chromium nitrate, bichromate, and chromate such as CrO_3 , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, $\text{Cr}(\text{Ac})_3$, $\text{Cr}(\text{C}_2\text{O}_4)_3$, CrCl_3 , and $\text{Cr}(\text{NO}_3)_3$.
8. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the content of the said inorganic chromium support, measured at the support weight, is 0.01 ~ 5.0wt%.
9. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the content of the said inorganic chromium support, measured at the support weight, is 0.05 ~ 1.5wt% for the better ones.
10. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that it is roasted at a temperature of 300 ~ 800 °C.

11. The feature of the preparation technique of a Ziegler-type catalyst applicable in the gas-phase method ethylene polymerization process lies in the fact that this preparation technique includes the following processes:
- (A) Have the inorganic chromium compound dissolved in distilled water or prepare a water solution from deionized water;
 - (B) Impregnate the inorganic oxide support such as the SiO_2 , Al_2O_3 , the surface of which contains the alkyl, into the solution prepared from the Step (A);
 - (C) Dry the solution in the Step (B) in the air to a free flow condition;
 - (D) Activate, in the oxygen-containing ambient, the particle in the Step (C) under the fluidization conditions;
 - (E) Put the midbody of the catalyst, which is activated in the Step (D), into the inert organic solvent medium; reduce it with an organic aluminum reducer in the inert ambient; dry it to a good flow condition, producing the catalyst;
12. The feature of the said preparation technique of the catalyst in the Item 11 of the Claims lies in the fact that, in activation, it takes 0.5 ~ 12 hours to activate at a temperature of 300 ~ 800 °C.
13. The feature of the said preparation technique of the catalyst in the Item 11 of the Claims lies in the fact that, in reduction, it takes 0.1 ~ 4 hours to contact at a temperature of 10 ~ 80 °C.

Explanations

A Ziegler-type Catalyst and its Preparation Technique, Which is Applicable in the Gas-phase Method Ethylene Polymerization Process

This invention relates to a Ziegler-type catalyst and its preparation technique, which is applicable in the gas-phase method ethylene polymerization process, and particularly the Ziegler-type chromium-containing solid catalyst and its preparation technique applicable in the gas-phase method ethylene polymerization process.

The Ziegler-type chromium-containing solid catalyst is one of the earlier types of successfully developed catalysts in the field of the ethylene polymerization. This type of the catalyst generally includes two categories: the inorganic chromium (oxidized chromium) and organic chromium. U.S. patent No. 2,825,721 published a catalyst of the Ziegler-type oxidized chromium. The water solution of such chromium compounds as chromium trioxide is used to impregnate the support. The catalyst, after being dried and roasted, is produced and is applicable in synthetic products with a narrower distribution of molecular weight. In comparison, oxidized chromium catalyst overcomes the weakness of organic chromium catalysts due to the complicated synthetic process of organic chromium with activation components. The advantage of its low cost is evident in producing inorganic-chromium type catalysts. However, the application scope of the inorganic chromium-type catalyst is limited due to the following shortcomings: the oxidized chromium-type catalyst itself requires a long time for polymerization to occur; the hydrogen peroxide is insensitive; the property of the copolymerization is poor; the melt index of the synthetic products is low; and the distribution of the molecular weight is narrow. Therefore, there are many improved types of inorganic chromium-type catalysts. U.S. Patent number 4,735,931 uses CO as a reducer to increase the melt index of the products, but it is still difficult to overcome the following problems: the length of time for polymerization for traditional oxidized chromium catalysts, their poor copolymerization characteristics, and narrow distribution of molecular weight. In U.S. patent No. 4,877,763 and U.S. patent No. 5,284,926, prior to the polymerization reaction, the micro organic aluminum and organic boron compounds are separately added into the reactor to increase activation of polymerization and the melt index of the products, and to improve the distribution of molecular weight. However, it complicates the process of the polymerization process to directly add the reducer of the organic metal compound into the reactor. Moreover, the time and amount of the reducer to be added must be strictly controlled and measured. In addition, the said improved catalyst is mainly for the ethylene polymerization process in the slurry process. It does not deal with the oxidized chromium-type catalyst applicable in the gas-phase method ethylene polymerization process.

The objective of this invention is to overcome the shortcomings of the said improved oxidized chromium-type catalysts and to provide a Ziegler-type solid catalyst, applicable in the gas-phase method ethylene polymerization process, of the high activation and the strong copolymerization properties.

Another objective of this invention is to provide the preparation technique of the Ziegler-type chromium catalyst applicable in the gas-phase method ethylene polymerization process.

To reach the above objectives, the outline of the technical scheme we adopt is as follows:

- (1) Have the inorganic chromium compound dissolved in distilled water or prepare a water solution of 0.01 ~ 5.0 mol/l from deionized water;
- (2) Put an inorganic oxide support such as SiO_2 and Al_2O_3 , the surface of which contains alkyl, into the solution with inorganic chromium and impregnate it for 5 ~ 10 hours at a temperature of 10 ~ 80°C. Measured by the weight of the support, the content of the chromium is 0.01 ~ 5.0wt% or, most preferably 0.05 ~ 1.5wt%.
- (3) Dry the solution in the Step (2) in the air for 5 ~ 48 hours or, most preferably, for 12 ~ 24 hours at an air temperature of 80 ~ 120°C to a free flow condition.
- (4) Activate, in an oxygen-containing ambient of 150 ~ 950°C, place the particle in the Step (3) under fluidization for 0.5 ~ 12 hours or, most preferably, for 1 ~ 8 hours at a temperature of 300 ~ 800°C.
- (5) Put the midbody of the catalyst, which is activated in the Step (4), into the inert organic solvent medium; reduce it with the organic reducer in an inert ambient for 0.1 ~ 4 hours at a temperature of 10 ~ 80°C; then dry it to a good flow condition in the inert air flow, producing the catalyst. The inert gases are the pure and high nitrogen, helium, or argon.

The chromium compound referred in this invention include the majority of inorganic chromium compounds such as CrO_3 , including chromium oxide, inorganic salt, acetate, oxalate, chromium nitrate, bichromate, and chromate.

The catalyst support of this invention adopts the difficult-to-melt inorganic oxide support, the surface of which contains alkyl, such as SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and TiO_2 . The better ones are those oxidized silica supports that have a ratio surface of 150 ~ 350 cm^3/g , an aperture of 10 ~ 50nm, and a particle size of 10 ~ 200 μm .

The organic reducer adopted in this invention is a metal organic compound, primarily the organic aluminum compound such as the triisobutyl aluminum, trimethyl aluminum, triethyl aluminum, ethoxyl diethyl aluminum, methyl aluminum oxysilane, ethyl aluminum oxysilane, butyl aluminum oxysilane, and other similar compounds. Its formula can be expressed as:



Whereas, R or R' is the alkyl of 1 ~ 20 carbon atoms. These two may be the same or different. The x or y is an integer ranging from 1 to 3. These two may be the same or different. The said organic metal compound may be used independently, or two or more may also be used together. The amount of the organic aluminum compound is related to the amount of the chromium-containing compound which is carried by the support. The Al/Cr ratio (the molar ratio) denotes its relative amount. The Al/Cr ratio is normally within the range of 0 ~ 50, while the better amount is within the range of 0.5 ~ 20. The objective of adding the organic aluminum compound is to reduce the high valence aluminum (+6), after being roasted, into the polymerization active

site with a series of different low valences, which is helpful to produce polyethylene resin of high density or medium density, with wider distribution of molecular weight.

The inert organic solvents adopted in this invention include saturated paraffins or pentane, isopentene, hexane, heptane, pure kerosene, and other similar paraffins; saturated cycloparaffins such as the cyclohexenyl, cyclopentane, dimethyl cyclopentane, methyl cyclohexenyl, and other similar cycloparaffins; arenes such as the benzene, methylbenzene, xylene, and other similar arenes; preferable solvents are isopentene, pentane, hexane, heptane, and cyclohexenyl.

The catalyst in this invention can be used for gas-phase polymerization reactions. The gas-phase polymerization reaction device can be either a gas-phase stir bed cauldron or a gas-phase fluidization bed reactor. Prior to polymerization, the catalyst can directly undertake the polymerization reaction without going through prepolymerization. The said homo-polymerization refers to polymerization of ethylene without having a copolymerization monomer. The said copolymerization refers to the copolymerization reaction of ethylene and α -alkene, which is aimed to reduce the density of polyethylene resin products. The adopted α -alkene refers to α -alkene that contains 3 ~ 20 carbon atoms, while the better ones are those α -alkenes that contain 3 ~ 8 carbon atoms, including propylene, 1-butene, 1-hexene, 4-methylpentene-1, and 1-octene. The temperature range of the polymerization is 20 ~ 150 °C, while the better one is 50 ~ 120 °C. The pressure of the polymerization reaction is 0.05 ~ 5MPa, while the better one is 0.1 ~ 3MPa.

In evaluating the catalyst, this invention uses a gas-phase stir bed cauldron and adopts the technique of gas-phase polymerization. The reactor is a high pressure cauldron made of stainless steel and with a volume of 1 liter. It has a cauldron cover that can be fixed with bolts and screws. The reactor is equipped with blenders, a flow conductor, a temperature control jacket, a pressure monitoring device, and tubes that lead the reaction gases, hydrogen, nitrogen, copolymerization monomer into the reactor.

During the polymerization reaction process, computers are used to control and measure temperature and pressure. The ethylene monomer is added through the mass flow meter. The radiotube is used to control the addition of the copolymerization monomer and hydrogen. The following steps are taken: have the cauldron under vacuum treatment for about 2 hours, during which pure and high nitrogen is impregnated multiple times and replaced 6 ~ 10 times; increase, through the thermostatic water baths, the temperature of the cauldron up to slightly below the reaction temperature; add the catalyst under the protection of the pure and high nitrogen; extract the nitrogen after dispersing it; add the ethylene to the pressure needed for the reaction; begin to keep track of time from the beginning of the reaction. The following formula is used to calculate the polymerization yield:

$$W_{\text{poly}} = (Q \cdot 60) / (t_{\text{poly}} \cdot W_{\text{cat}}), \quad \text{g} \cdot \text{PE} / \text{g} \cdot \text{Cat} \cdot \text{h}$$

Whereas, Q is the yield (g) of the polymer within the time t (minutes) of the polymerization reaction, W_{cat} is the amount of catalyst. Once the polymerization reaction is completed, the reaction is terminated by discharging reaction gases.

The extraordinary features of this invention are as follows:

- (1) This catalyst uses the inorganic chromium compound as raw a material, which is cheap to buy and easy to obtain, so the cost is lower.
- (2) The organic aluminum compound is used as the reducer, to greatly reduce the time of the reduction; the need for high temperatures is reduced, which saves time and energy.
- (3) In the evaluation, this catalyst adopts the gas-phase method, which is applicable in the gas-phase fluidization bed process, with the advantages of the less investment, lower energy consumption, and lack of waste.

In order to better elaborate this invention, we present the following examples; however, this invention is not limited to the following examples.

For the polymer produced in the examples, melt flow velocity is determined in accordance with ASTM D 1238-65T, and the density is determined in accordance with ASTM D 1505-68.

Example 1

Put 0.5g CrO_3 into a millimeter small mouth flask, adding distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davision 955 silica gels into the 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution, and add it into the flask; after agitating it finely, dry it at an air temperature of 80 ~ 120°C for 12 hours to a good flow condition; put into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C, and then 4 hours at 600°C; at last, switch into the pure and high nitrogen, which is dewatered through the 13X molecular sieves, and keep it for 1 hour at the 600°C; under the fluidization and in the nitrogen, cool it down to the room temperature and take it out before use. Under the protection of the said pure and high nitrogen, add 1g of the said support CrO_3 silica gels; then add 0.35ml 25% (m/m) hexane solution of the ethoxyl diethyl aluminum; treat it for 1 hour under the condition of the tight-controlled agitation; then use the dry pure and high nitrogen to blow away the solvent, producing the powder catalyst with 0.25wt% of the amount of chromium contained with an Al/Cr ratio of 3.

Examples 2 ~ 4

The preparation technique of the catalyst in the examples 2 ~ 4 is similar to that in the example 1. The difference is that examples 2 ~ 4 respectively use triethyl aluminum, tri-butyl aluminum, and methyl aluminum oxysilane to get the powder catalyst with 0.25wt% of the amount of the chromium contained with an Al/Cr ratio of 3.

Subject Example 1

Put 0.5g CrO_3 into a 100ml small mouth flask, add distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davison 955 silica gels into a 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution and add it into the flask; after agitating it finely, dry it at an air temperature of 80 ~ 120°C for 12 hours to a better flow condition; put into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C and then 4 hours at 600°C; finally, switch it into the pure and high nitrogen, which is dewatered through 13X molecular sieves, and keep it for 1 hour at the 600°C; under the fluidization and in the nitrogen, cool it down to room temperature and take it out, producing a traditional oxidized chromium catalyst.

Subject Example 2

Put 0.5g CrO_3 into the 100ml small mouth flask, adding distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davison 955 silica gels into the 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution and add it into the flask; after agitating it finely, dry it at a air temperature of 80 ~ 120°C for 12 hours to a better flow condition; put it into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce the dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C and then 4 hours at 600°C; and then, switch it into the pure and high nitrogen, which is dewatered through 13X molecular sieves, and lower the temperature down to 350°C; then switch it into CO gas at 350°C and reduce it for 2 hours; finally, switch it into the said pure and high nitrogen and maintain for 1 hour; after that, under the fluidization and in the nitrogen, cool it down to room temperature and take it out before use, thus producing the CO reduction chromium catalyst.

The catalyst made from the examples 1 ~ 4 and from the subject examples 1 and 2 is separately used for polymerization reactions with the results presented in the Table 1.

Examples 5 ~ 7

The preparation technique of the catalyst in examples 5 ~ 7 is similar to that in the example 1. The difference is that in examples 5 ~ 7, the Al/Cr ratio (molar /molar) is respectively 1, 6, and 10 in producing the powder catalyst.

Examples 8 ~ 10

The preparation technique of the catalyst in examples 8 ~ 10 is similar to that in example 1. The difference is that in the examples 8 ~ 10, the amount of the chromium Cr wt% is respectively 0.1, 0.15, and 0.5, in producing the powder catalyst.

Examples 11 ~ 13

The preparation technique of the catalyst in examples 11 ~ 13 is similar to that in example 1. The difference is that in examples 11 ~ 13, the activating temperature is respectively 400°C, 500°C, and 800°C, in producing the powder catalyst.

The catalyst made from the examples 5 ~ 13 is separately used for polymerization reaction with the results presented in the Table 2.

Examples 14 ~ 16

Use the catalyst produced in example 1 and follow the evaluation methods provided in this invention, with the H_2/C_2H_4 ratio as 0.02, 0.06, and 0.10, respectively; weigh and test the powder of the polyethylene products with the results presented in the Table 3.

Examples 17 ~ 19

Use the catalyst produced in the example 1 and follow the evaluation methods provided in this invention, with the C_3H_6/C_2H_4 ratio as 0.006, 0.012, and 0.020, respectively; weigh and test the powder of the polyethylene products with the results presented in the Table 4.

Examples 20 ~ 22

Use the catalyst produced in the example 1 and follow the evaluation methods provided in this invention, with -butene as the copolymerization monomer and the C_4H_8/C_2H_4 ratio as 0.006, 0.012, and 0.020, respectively; weigh and test the powder of the resulting polyethylene products with the results presented in the Table 5.

Table 1

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	Catalyst		Polymer Yield	$I_{21.5}$	Density
	Cr, wt%	Al/Cr	gPE/gCat.h	g/10min	g/cm ³
Example 1	0.25	3	236	25.31	0.9582
Example 2	0.25	3	285	3.59	0.9587
Example 3	0.25	3	379	3.56	0.9598
Example 4	0.25	3	481	5.25	0.9606
Subject Example 1	0.25	3	186	1.54	0.9631
Subject Example 2	0.25	0	202	6.46	0.9648

Table 2

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	Catalyst				Polymer Yield	I _{21.5}	Density
	Cr, wt%	Reducer	Al/Cr	Activating Temperature °C	gPE/gCat.h	g/10min	g/cm ³
Example 5	0.25	EtOAlET ₂	1	600	221	5.32	0.9612
Example 6	0.25	EtOAlET ₂	6	600	263	23.86	0.9597
Example 7	0.25	EtOAlET ₂	10	600	235	22.76	0.9586
Example 8	0.10	EtOAlET ₂	3	600	68	3.91	0.9588
Example 9	0.15	EtOAlET ₂	3	600	153	8.27	0.9593
Example 10	0.50	EtOAlET ₂	3	600	287	32.93	0.9635
Example 11	0.25	EtOAlET ₂	3	400	121	11.82	0.9596
Example 12	0.25	EtOAlET ₂	3	500	198	17.08	0.9598
Example 13	0.25	EtOAlET ₂	3	800	336	58.18	0.9606

Table 3

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	H ₂ /C ₂ H ₄ ratio	Ethylene Partial Pressure MPa	Nitrogen Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 14	0.02	1.078	0.022	228	35.63	0.9524
Example 15	0.06	1.034	0.066	216	78.21	0.9512
Example 16	0.10	1.990	0.110	234	99.39	0.9503

Table 4

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	C ₃ /C ₂ H ₄ Ratio	Ethylene Partial Pressure MPa	Propylene Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 17	0.06	1.093	0.007	235	38.69	0.9482
Example 18	0.012	1.087	0.013	226	42.64	0.9435
Example 19	0.020	1.078	0.022	243	45.27	0.9386

Table 5

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	C ₄ /C ₂ H ₄ Ratio	Ethylene Partial Pressure MPa	Polymerization Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 20	0.006	1.093	0.007	226	41.32	0.9468
Example 21	0.012	1.087	0.013	265	46.61	0.9413
Example 22	0.020	1.078	0.022	249	49.26	0.9364

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[54]发明名称 一种适用于气相法乙烯聚合工艺的负载型
催化剂及其制备方法

[57]摘要

本发明涉及一种适用于气相法乙烯聚合工艺的负载型催化剂及其制备方法。该催化剂具有活性高、共聚性能良好、产品分子量分布宽的特点,可以用于乙烯气相均聚以及 α -烯烃共聚生产低压高密度聚乙烯或中低密度聚乙烯。

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权利要求书

1. 一种适用于气相法乙烯聚合工艺的负载型催化剂,包括将表面含羟基的难熔的无机氧化物载体浸渍于无机铬化合物水溶液中,经干燥、焙烧、还原得到催化剂,其特征在于采用有机铝化合物作为还原剂。

2. 如权利要求1所述的催化剂,其特征在于所述的还原剂为具有下列通式的有机铝化合物:



其中R或R'为1~20碳原子的烷基,二者可以相同或不同;x或y为1~3的整数,二者可以相同或不同。

3. 如权利要求1所述的催化剂,其特征在于所述的有机铝还原剂为有机铝化合物,如 AlR_3 、 ROIR'_x 。

4. 如权利要求1所述的催化剂,其特征在于所述的有机铝还原剂也可以为烷基铝化合物的部分水解物,如MAO、EAO、BAO、i-BAO、EBAO。5. 如权利要求1所述的催化剂,其特征在于所述的无机氧化物载体为 SiO_2 、 Al_2O_3 、 $\text{SiO}_2-\text{Al}_2\text{O}_3$ 、 TiO_2 。

6. 如权利要求1所述的催化剂,其特征在于所述的无机氧化物载体较好的是氧化硅载体。

7. 如权利要求1所述的催化剂,其特征在于所述的无机铬化合物包括铬的氧化物、无机盐、醋酸盐、草酸盐、羧酸盐、重铬酸盐、铬酸盐如 CrO_3 、 $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ 、 $\text{Cr}(\text{Ac})_3$ 、 $\text{Cr}(\text{C}_2\text{O}_4)_3$ 、 CrCl_3 、 $\text{Cr}(\text{NO}_3)_3$ 。

8. 如权利要求1所述的催化剂,其特征在于所述的无机铬的含量以载体质量计为0.01~5.0wt%。

9. 如权利要求1所述的催化剂,其特征在于所述的无机铬的含量以载体质量计,较好为0.05~1.5wt%。

10. 如权利要求1所述的催化剂,其特征在于在300~800℃的温度条件下进行焙烧。

11. 一种适用于气相法乙烯聚合工艺的负载型催化剂的制备方法,其特征
在于该方法分下列步骤进行:

(A)将无机铬化合物溶解在蒸馏水或去离子水中配制成水溶液,

(B)将表面含羟基的无机氧化物载体如 SiO_2 、 Al_2O_3 浸渍于步骤(A)的溶
液中,

(C)将步骤(B)的溶液在空气气氛中进行干燥至自由流动状态,

(D)在含氧气氛中将步骤(C)的颗粒在流化状态下进行活化,

(E)将步骤(D)活化好的催化剂中间体放入惰性有机溶剂介质中在惰性气
氛下用有机铝还原剂进行还原,干燥呈良好流动状态,制得催化剂。

12. 如权利要求 11 所述的催化剂的制备方法,其特征在于进行活化时,在
 $300\sim 800^\circ\text{C}$ 下活化 0.5~12 小时。

13. 如权利要求 11 所述的催化剂的制备方法,其特征在于进行还原时,在
 $10\sim 80^\circ\text{C}$ 下,接触 0.1~4 小时。

说明书

一种适用于气相法乙烯聚合工艺的负载型催化剂及其制备方法

本发明涉及一种适用于乙烯聚合工艺的催化剂及其制备方法,特别是涉及一种适用于气相法乙烯聚合工艺的负载型含铬固体催化剂及其制备方法。

负载型含铬催化剂是乙烯聚合领域较早开发成功的催化剂类型。这类催化剂一般包括无机铬系(氧化铬系)和有机铬系两个系列。美国专利 2,825,721 公开的是负载型氧化铬催化剂,用三氧化铬等铬的化合物的水溶液浸渍载体,经干燥、焙烧得到,适用于合成分子量分布较窄的产品。相比较而言,无机铬系催化剂由于克服了有机铬系催化剂中活性组份有机铬合成工艺复杂的缺点,催化剂成本低的优势非常明显,但由于氧化铬催化剂本身具有聚合引发时间长,氢调不敏感,共聚性能差,合成产品熔融指数低,分子量分布窄等缺点,也限制了其应用范围。于是出现了许多改进型氧化铬催化剂。美国专利 4,735,931 采用 CO 作还原剂,提高了产品熔融指数,但仍难以克服传统氧化铬催化剂聚合引发时间长,共聚性能差,分子量分布窄等缺点;美国专利 4,877,763 和美国专利 5,284,926 是在聚合反应前分别向反应器中加入微量的有机铝和有机硼化合物,提高了聚合活性和产品熔融指数,改善了分子量分布,但直接向反应器中加入有机金属化合物还原剂使聚合工艺过程复杂化,而且还原剂的加入时间和加入量要严格控制 and 计量,并且上述改进型催化剂主要是针对淤浆法乙烯聚合工艺,对适用于气相法乙烯聚合工艺的氧化铬催化剂并未涉及。

本发明的目的是克服上述改进型氧化铬催化剂的缺点,提供一种适用于气相法乙烯聚合工艺的活性高、共聚性能良好的负载型固体催化剂。

本发明的另一个目的是提供适用于气相法乙烯聚合工艺的负载型铬系催化剂的制备方法。

为了达到上述目的,我们采用的技术方案概述如下:

(1)将无机铬化合物溶解在蒸馏水或去离子水中配制成 0.01~5.0 mol/l 的溶液。

(2)将表面含羟基的无机氧化物载体如 SiO_2 , Al_2O_3 放入含有无机铬的水溶液中,在 $10\sim 80^\circ\text{C}$ 的温度下浸渍 $5\sim 10$ 小时,以载体质量计,铬含量为 $0.01\sim 5.0\text{wt}\%$,最好是 $0.05\sim 1.5\text{wt}\%$ 。

(3)将步骤(2)的溶液在 $80\sim 120^\circ\text{C}$ 的空气气氛中干燥 $5\sim 48$ 小时,最好干燥 $12\sim 24$ 小时,干燥到自由流动状态。

(4)在 $150\sim 950^\circ\text{C}$ 的含氧气氛中,在流化状态下将步骤(3)的颗粒活化 $0.5\sim 12$ 小时,最好在 $300\sim 800^\circ\text{C}$ 温度条件下活化 $1\sim 8$ 小时。

(5)将步骤(4)所得的活化好的催化剂中间体放入惰性有机溶剂介质中在惰性气氛下用有机还原剂在 $10\sim 80^\circ\text{C}$ 下接触 $0.1\sim 4$ 小时进行还原,然后在惰性气流中干燥呈良好流动状态制得催化剂,惰性气氛为高纯氮气、氦气或氢气。

本发明所述及的铬化合物是包括 CrO_3 在内的大部分无机铬化合物,其中包括铬的氧化物、无机盐、醋酸盐、草酸盐、羧酸盐、重铬酸盐、铬酸盐等等。

本发明的催化剂载体采用表面含羟基的难熔的无机氧化物载体,如 SiO_2 、 Al_2O_3 、 $\text{SiO}_2-\text{Al}_2\text{O}_3$ 、 TiO_2 等,较好的是具有比表面 $150\sim 350\text{cm}^2/\text{g}$,孔径 $10\sim 50\text{nm}$,颗粒尺寸 $10\sim 200\mu\text{m}$ 的氧化硅载体。

本发明所采用的有机还原剂为金属有机化合物,主要是有机铝化合物,如三异丁基铝、三甲基铝、三乙基铝、乙氧基二乙基铝、甲基铝氧烷、乙基铝氧烷、丁基铝氧烷等等,以及其它类似化合物,其通式可表达为:



其中 R 或 R' 为 $1\sim 20$ 碳原子的烷基,二者可以相同或不同。x 或 y 为 $1\sim 3$ 的整数,二者可以相同或不同。上述有机金属化合物可以一种单独使用,也可以两种或两种以上共同使用,有机铝化合物的用量与载体上所负载的含铬化合物的量有关。用 Al/Cr 比(摩尔比)表示其相对量,一般 Al/Cr 比在 $0\sim 50$ 之间,较好的用量在 $0.5\sim 20$ 之间,加入有机铝化合物的目的在于将焙烧后的高价铬(+6)还原成为具有一系列不同低价态的聚合活性位,有利于制取高密度或中密度的分子量分布较宽的聚乙烯树脂。

本发明所采用的惰性有机溶剂包括饱和烷烃或戊烷、异戊烷、己烷、庚烷、纯煤油及其它类似烷烃;饱和的环烷烃如环己烷、环戊烷、二甲基环戊烷、甲基

环己烷及其它类似环烷烃,芳烃,如苯、甲苯、二甲苯及其它类似芳烃,优选的溶剂为异戊烷、戊烷、己烷、庚烷和环己烷。

采用本发明的催化剂可以进行气相聚合反应,所采用的气相聚合反应装置可以是气相搅拌床反应釜或气相流化床反应器。在聚合之前催化剂不需要预聚合即可进行聚合反应。所述均聚指在没有共聚单体的情况下乙烯进行聚合。所述共聚指乙烯与 α -烯烃进行的共聚合反应,目的是降低聚乙烯树脂产品的密度,所采用的 α -烯烃是指含有3~20个碳原子的 α -烯烃,较好的是含有3~8个碳原子的 α -烯烃。其中包括丙烯、丁烯-1、己烯-1、4-甲基戊烯-1、辛烯-1等等。聚合温度范围为20~150℃,较好的是50~120℃,聚合反应压力为0.05~5MPa,较好的为0.1~3MPa。

本发明在实验室评价催化剂采用气相搅拌床反应釜进行气相聚合的方法。反应器为不锈钢制成的体积为1升的高压釜,带有可用螺栓固定的釜盖,反应器备有搅拌桨、导流器、控温夹套、测温装置、测压装置以及将反应气体和氢气、氮气和共聚单体导入反应器的导管。

聚合反应中温度和压力采用计算机控制和计量,乙烯单体通过质量流量计加入,共聚单体和氢气加量由电磁阀控制。按下述步骤进行,将反应釜抽真空处理约2小时,期间多次充入高纯氮气置换6~10次,通过恒温水浴将反应釜升温到稍低于反应温度,在高纯氮气保护下加入催化剂,使其分散后抽去氮气,加入乙烯至反应所需压力,反应开始计时。按以下公式计算聚合收率:

$$W_{\text{poly}} = (Q \cdot 60) / (t_{\text{poly}} \cdot W_{\text{cat}}), \quad \text{g. PE/g. Cat. h}$$

其中Q为在聚合反应时间t(分钟)内聚合物的产率(g), W_{cat} 为催化剂用量。聚合反应结束,排放掉反应气终止反应。

本发明的突出特点是:

- (1)本催化剂所用原料无机铬化合物价廉易得,成本较低。
- (2)采用有机铝化合物作还原剂,还原时间大大缩短,且不需高温,节约了时间和能量。
- (3)本催化剂采用气相法评价,适用于气相流化床工艺,具有投资少,能耗低,无三废等突出优点。

为了更好地说明本发明,我们特列举下述实施例,但本发明并不限于下述实施例。

实施例中制得的聚合物的熔体流动速率依据 ASTM D 1238—65T 测定,密度依据 ASTM D 1505—68 进行测定。

实施例 1

将 0.5g CrO_3 放入毫升容量瓶中,加入蒸馏水或去离子水配制成 0.05mol/l 的水溶液待用。称取 10g Davison 955 硅胶放入 100ml 烧杯中,然后用移液管移取 9.62ml 的 0.05mol/l 的上述水溶液加入到烧杯中,搅匀后在空气中 80~120℃ 下干燥 12 小时呈良好流动状态,再放入 $\Phi 30 \times 500\text{mm}$ 的底部焊有微孔烧结石英分布板的石英流化床,通入经 13X 分子筛脱水的干燥空气,使其呈流化状态下进一步脱水,其升温过程为 200℃ 2 小时,然后 600℃ 4 小时,最后在 600℃ 下切换为经 13X 分子筛脱水的高纯氮气维持 1 小时后在流化状态下氮气气氛中冷却至室温取出待用。在上述高纯氮气保护下加入 1g 上述负载 CrO_3 的硅胶,然后加入 0.35ml 25%(m/m) 的乙氧基二乙基铝的己烷溶液,在密闭搅拌的情况下处理 1 小时,而后用干燥高纯氮气吹扫除尽溶剂,制成含铬量为 0.25wt%, Al/Cr 比为 3 的粉状催化剂。

实施例 2~4

催化剂制备方法与实施例 1 相似,其区别在于实施例 2~4 分别采用三乙基铝、三特丁基铝和甲基铝氧烷,得到含铬量为 0.25wt%, Al/Cr 比为 3 的粉状催化剂。

对比例 1

将 0.5g CrO_3 放入 100 ml 容量瓶中,加入蒸馏水或去离子水配制成 0.05 mol/l 的水溶液待用。称取 10 g Davison 955 硅胶放入 100 ml 烧杯中,然后用移液管移取 9.62ml 的 0.05 mol/l 的上述水溶液加入到烧杯中,搅匀后在空气中 80~120℃ 下干燥 12 小时呈较好流动状态,再放入 $\Phi 30 \times 500\text{mm}$ 的底部焊有微孔烧结石英分布板的石英流化床,通入经 13X 分子筛脱水的干燥空气,使其呈流化状态下进一步脱水,其升温过程为 200℃ 2 小时,然后 600℃ 4 小时,最后在 600℃ 下切换为经 13X 脱水的高纯氮气维持 1 小时后在流化状态下氮

气氛中冷却至室温取出,得到传统的氧化铬催化剂。

对比例 2

将 0.5g CrO_3 放入 100ml 容量瓶中,加入蒸馏水或去离子水配制成 0.05 mol/l 的水溶液待用。称取 10 g Davison 955 硅胶放入 100 ml 烧杯中,然后用移液管移取 9.62 ml 的 0.05mol/l 的上述水溶液加入到烧杯中,搅匀后在空气中 80~120℃ 下干燥 12 小时呈较好流动状态,再放入 $\Phi 30 \times 500\text{mm}$ 的底部焊有微孔烧结石英分布板的石英流化床,通入经 13X 分子筛脱水的干燥空气,使其呈流化状态下进一步脱水,其升温过程为 200℃ 2 小时,600℃ 4 小时,然后切换为经 13X 脱水的高纯氮气,降温至 350℃,再切换成 CO 气体 350℃ 还原 2.0 小时,最后切换为上述高纯氮气维持 1 小时后在流化状态下氮气气氛中冷却至室温取出待用,得到 CO 还原型铬催化剂。

现将分别用实施例 1~4 和对比例 1 及对比例 2 所制得催化剂进行聚合反应,所得结果列于表 1。

实施例 5~7

催化剂的制备方法与实施例 1 相似,其区别在于实施例 5~7 中 Al/Cr 比(摩尔/摩尔)分别为 1,6,10,得到粉状催化剂。

实施例 8~10

催化剂制备方法与实施例 1 相似,其区别在于实施例 8~10 中含铬量 Cr wt\% ,分别为 0.1,0.15,0.5,得到粉状催化剂。

实施例 11~13

催化剂的制备方法与实施例 1 相似,其区别在于实施例 11~13 中,活化温度分别为 400℃,500℃,800℃,得到粉状催化剂。

现将分别用实施例 5~13 所得的催化剂进行聚合反应,所得结果列于表 2。

实施例 14~16

采用实施例 1 制备的催化剂,按本发明提供的评价方法,其中 $\text{H}_2/\text{C}_2\text{H}_4$ 比分别为 0.02、0.06、0.10,将得到的聚乙烯产品粉末称重、测试。所得结果列于表 3。

实施例 17~19

采用实施例 1 制备的催化剂,按本发明所提供的评价方法,其中 C_3H_6/C_2H_4 比分别为 0.006,0.012,0.020,将得到的聚乙烯产品粉末称重、测试,所得结果列于表 4。

实施例 20~22

采用实施例 1 制备的催化剂,按本发明所提供的评价方法,其中丁烯-1 作为共聚单体, C_4H_8/C_2H_4 比分别为 0.006,0.012,0.020,将得到的聚乙烯产品粉末称重、测试,所得结果列于表 5。

表 1

聚合条件,反应温度为 95℃,反应压力为 1.100MPa,反应时间为 60min。

编 号	催化 剂		聚合物收率	$I_{m.s}$	密度
	Cr,wt%	Al/Cr	gPE/gCat. h	g/10min	g/cm ³
实施例 1	0.25	3	236	25.31	0.9582
实施例 2	0.25	3	285	3.59	0.9587
实施例 3	0.25	3	379	3.56	0.9598
实施例 4	0.25	3	481	5.25	0.9606
对比例 1	0.25	3	186	1.54	0.9631
对比例 2	0.25	0	202	6.46	0.9648

表 2

聚合条件,反应温度为 95℃,反应压力为 1.100MPa,反应时间为 60min。

编 号	催 化 剂				聚合物收率 gPE/gCat. h	$I_{n.}$ g/10min	密度 g/cm ³
	Cr, wt%	还原剂	Al/Cr	活化温度, °C			
实施例 5	0.25	EtOAlEt ₂	1	600	221	5.32	0.9612
实施例 6	0.25	EtOAlEt ₂	6	600	263	23.86	0.9597
实施例 7	0.25	EtOAlEt ₂	10	600	235	22.76	0.9586
实施例 8	0.10	EtOAlEt ₂	3	600	68	3.91	0.9588
实施例 9	0.15	EtOAlEt ₂	3	600	153	8.27	0.9593
实施例 10	0.50	EtOAlEt ₂	3	600	287	32.93	0.9635
实施例 11	0.25	EtOAlEt ₂	3	400	121	11.82	0.9596
实施例 12	0.25	EtOAlEt ₂	3	500	198	17.08	0.9598
实施例 13	0.25	EtOAlEt ₂	3	800	336	58.18	0.9606

表 3

聚合条件,反应温度为 95℃,反应压力为 1.100MPa,反应时间为 60min。

编 号	H ₂ /C ₂ H ₄ 比	乙烯分压 MPa	氢气分压 MPa	聚合物收率 gPE/gCat. h	$I_{n.}$ g/10min	密度 g/cm ³
实施例 14	0.02	1.078	0.022	228	35.63	0.9524
实施例 15	0.06	1.034	0.066	216	78.21	0.9512
实施例 16	0.10	0.990	0.110	234	99.39	0.9503

表 4

聚合条件,反应温度为 95℃,反应压力为 1.100MPa,反应时间为 60min。

编 号	C ₃ /C ₂ H ₄ 比	乙烯分压 MPa	丙烯分压 MPa	聚合物收率 gPE/gCat. h	$I_{n.}$ g/10min	密度 g/cm ³
实施例 17	0.06	1.093	0.007	235	38.69	0.9482
实施例 18	0.012	1.087	0.013	226	42.64	0.9435
实施例 19	0.020	1.078	0.022	243	45.27	0.9386

97.11.10

表 5

聚合条件:反应温度为 95℃,反应压力为 1.100MPa,反应时间为 60min.

编 号	C_1^*/C_2H_4 比	乙烯分压 MPa	丁烯分压 MPa	聚合物收率 gPE/gCat. h	$I_{n.s}$ g/10min	密度 g/cm ³
实施例 20	0.006	1.093	0.007	226	41.32	0.9468
实施例 21	0.012	1.087	0.013	265	46.61	0.9413
实施例 22	0.020	1.078	0.022	249	49.26	0.9364